

Technical Background Document:  
Mercury Wastes  
Evaluation of Treatment of Bulk Elemental Mercury  
Final Report

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## Evaluation of Treatment of Bulk Elemental Mercury

### Executive Summary

The Environmental Protection Agency (EPA) and Department of Energy (DOE) have collaborated on a series of studies to evaluate the effectiveness of treatment technologies at stabilizing wastes containing large concentrations of mercury. In addition to mercury-contaminated wastes, the disposal of bulk elemental mercury is of concern because of the excess quantity of mercury in the Defense Logistics Agency (DLA) stockpile.

The study described in this report was designed to assist in evaluation of options for disposition of the inventory, by providing information on the ability of current technologies to convert elemental mercury (or wastes with large components of elemental mercury) into a stable waste form for disposal. The study evaluated the effectiveness of three technologies at stabilization of bulk elemental mercury. Bulk elemental mercury was treated by each vendor, and the treated waste forms evaluated for mercury leachability, using both the TCLP and a novel, automated, constant-pH leaching protocol. Constant pH leaching was conducted at pH 2, 4, 6, 8, 10, and 12 for 14 days at each pH.

The report provides descriptions of the study plan and the treatment processes, as well as detailed discussions of the leaching results. The leaching data presented demonstrate that the stability of the mercury in the treated waste forms varies widely across the pH range tested. Clearly, the stability of mercury in these treated waste forms will be highly dependant on the disposal conditions. The combination of site-specific disposal conditions and appropriate treatment technology must be considered as decisions are made about disposal of waste bulk elemental mercury.

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## 1. Introduction

The Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) require the EPA to establish treatment standards for all listed and characteristic hazardous wastes destined for land disposal. After the effective date of a restriction, wastes that do not meet the Land Disposal Restrictions (LDR) treatment standards are prohibited from land disposal.

The LDR treatment standards for the six waste codes (D009, K071, K106, P065, P091, and U151) which contain mercury as the primary hazardous constituent (Mercury Wastes) were promulgated in the Third LDR Rule (55 FR 22520, June 1, 1990). Some of these standards were revised when EPA promulgated Universal Treatment Standards in the Phase II LDR Rule (59 FR 47980, September 19, 1994). Since these rules were promulgated, however, the Agency has become aware of information and data which indicate that the treatment standards for some categories of these wastes may be inappropriate and warrant further review.

### 1.1 Disposal Options for Wastes Containing > 260 mg/kg Total Mercury

Under the existing LDRs, treatment by stabilization and disposal is not an available option for most wastes containing greater than 260 mg/kg total mercury (high mercury wastes). The reasons given in the 3rd LDR rule for this regulation are that, "EPA's data for untreated mercury wastes being retorted/roasted domestically show minimum concentrations of mercury up to 255 mg/kg," and that "There is a strong preference in the land disposal restrictions legislation for treatment standards to be based on recovery where possible." The technical background document for mercury wastes also cited data from attempts to treat K106 sludge containing 25.9 g/kg of total mercury using conventional metal-stabilizing agents (cement, kiln dust, lime/fly ash), indicating that the leachability of the waste was actually increased by the process.

Mercury is a high-priority chemical at EPA. It is one of twelve Persistent, Bioaccumulative and Toxic Chemicals (PBT) targeted in the U.S. Bi-National Strategy between the U.S. and Canada and is included in EPA's PBT Strategy. There are also efforts in the Agency to reduce mercury consumption and to take mercury out of circulation to minimize air emissions. For these reasons, it appears that the general preference for recovery over immobilization may not be appropriate for some categories of mercury wastes. In addition, various commenters and petitioners have submitted data indicating that wastes containing concentrations well above 260 mg/kg may be effectively stabilized. Therefore, EPA has decided to revisit the issue of mercury stabilization by gathering currently available performance data, possibly conducting new stabilization research, and investigating the long-term potential for oxidation or vaporization of land disposed mercury.

## 1.2 Wastes which are not directly amenable to roasting and retorting

Retorting or roasting for recovery (RMERC) is currently required for inorganic high mercury wastes. Commenters and petitioners have asserted that many subcategories of mercury wastes (e.g., inorganic salts, corrosive wastes, incineration residues, wastewater treatment residues) are not directly amenable to RMERC treatment, and are not accepted by commercial retorting facilities. Although EPA's general position has been that those nonamenable subcategories can be pretreated to make recovery possible, current management practices indicate that this position may be impractical and unrealistic. Therefore, EPA has decided to investigate alternative treatment technologies to roasting and retorting for high-mercury wastes.

## 1.3 Incineration of Mercury Wastes

Incineration (IMERC) is currently either required or allowed as an alternative to RMERC for organic high mercury wastes. The rationale for this standard given in the 3rd rule is that IMERC will destroy the organic component of organo-mercury complexes or mixtures, so that the "valuable mercury" present in the waste can be subsequently recovered from the incineration residuals (e.g., ash, baghouse dust, sludge from treated scrubber water). However, given the high volatility of mercury, it is reasonable to assume that both mercury and organo-mercury compounds will be vaporized by incineration rather than remain in the ash. Although some of this mercury will be captured by air pollution controls, the rest will be lost to the atmosphere. Furthermore, evaluation of current waste management practices indicates that incineration residuals are in fact not being treated for mercury recovery. Therefore, the Agency has decided to further investigate whether treatment alternatives exist for mercury wastes that might currently be going to incinerators for treatment.

## Elemental Mercury Waste Project Report

The purpose of this report is to provide an evaluation of the effectiveness of commercially available stabilization technologies on elemental mercury. The Department of Defense has maintained a huge inventory of mercury for many years. However, the DoD has determined that they will not need the volumes in the inventory. The DoD is preparing an environmental impact analysis of the options for disposition of the inventory. The options include sale, storage by other governmental agencies, and disposal. This report is designed to assist in identifying the proper methods of safe

## 2. Background

The Resource Conservation and Recovery Act (RCRA)<sup>1</sup> defines several categories of mercury wastes, each of which has a defined technology or concentration-based treatment standard, or universal treatment standard (UTS). RCRA defines mercury hazardous wastes as any waste that has a TCLP value for mercury of 0.2 mg/L or greater. Three of these categories, all nonwastewaters, fall within the scope of this report on new technologies to treat mercury-contaminated wastes:

- Wastes as elemental mercury;
- Hazardous wastes with less than 260 mg/kg [parts per million (ppm)] mercury; and
- Hazardous wastes with 260 ppm or more of mercury.

### 2.1 Current Treatment Methods

While this report deals specifically with the first category—waste elemental mercury—the other two categories will be discussed briefly so that the full range of mercury treatment challenges can be understood. The current treatment requirements for these three categories are as follows:

- Waste as elemental mercury—RCRA identifies amalgamation (AMLGM) as the treatment standard for elemental mercury contaminated with radioactive materials.
- Waste with < 260 ppm mercury—No specific treatment method is specified for hazardous wastes containing <260 ppm. However, RCRA regulations require that such wastes that exceed a TCLP mercury concentration of 0.20 mg/L be treated by a suitable method to meet the toxicity characteristic leaching procedure (TCLP)<sup>2</sup> limit for mercury of 0.20 mg/L.
- Waste with  $\geq$  260 ppm mercury—For hazardous wastes with mercury contaminant concentrations  $\geq$  260 ppm *and* RCRA-regulated organic contaminants (other than incinerator residues), incineration or retorting (IMERC or RMERC) is the treatment standard. For wastes with mercury contaminant concentrations  $\geq$  260 ppm that are inorganic, including incinerator and retort residues, RMERC is the treatment standard.

EPA's hazardous waste classification system identifies six categories of mercury-bearing wastes, each of which has a separate RCRA waste code. **Table 2-1** shows the six mercury waste codes and a brief description adapted from the May 28, 1999 proposed rule:

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<sup>1</sup> 40 CFR 268.40

<sup>2</sup> This procedure is described in Method 1311 of U.S. Environmental Protection Agency (EPA) Publication SW-846.

Table 2-1  
RCRA Codes for Wastes that Contain Mercury

Waste Code	Description
<b>D009—Characteristic Mercury Wastes</b>	D009 wastes are extremely variable in composition, and depend on the industry and process that generate the waste. Some of the more common types of D009 wastes include miscellaneous wastes from chlor-alkali production facilities (especially cell room trench sludge and activated carbon for liquid or gas purification), used fluorescent lamps, batteries, switches, and thermometers. D009 wastes are also generated in the production of organomercury compounds for fungicide/bactericide and pharmaceutical uses, and during organic chemicals manufacturing where mercuric chloride catalyst is used.*
<b>K071—Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used</b>	K071 wastes are generated by the chlor-alkali industry in the mercury cell process. In this process, sodium chloride is dissolved to form a saturated brine solution. The brine solution is purified by precipitation, using hydroxides, carbonates, or sulfates. The precipitate is dewatered to form K071 wastes, while the purified brine continues in the process. The depleted solution from the mercury cell is ultimately recycled to the initial step of the process.
<b>K106—Wastewater treatment sludge from the mercury cell process in chlorine production</b>	Like K071 wastes, K106 wastes are generated from chlorine production using the mercury cell process. Effluent from the mercury cell includes spent brine, a portion of which is recycled and a portion of which is purged to wastewater treatment. Other plant area wastewaters (e.g., stormwater, washdown waters) are also typically sent to this treatment system. The wastewater treatment process generates a sludge through precipitation and filtering, which is K106 waste. The mercury concentration in K106 waste is consistently greater than 260 mg/kg and therefore retorting is a required technology for this waste.
<b>P065—Mercury fulminate</b>	P065 wastes consist of discarded mercury fulminate product, off-specification mercury fulminate product, and container or spill residues thereof.
<b>P092—Phenylmercury acetate</b>	P092 wastes consist of discarded phenylmercury acetate product, off-specification phenylmercury acetate product, and container or spill residues thereof.
<b>U151—Mercury</b>	U151 wastes consist of discarded elemental mercury product, off-specification metallic mercury product, and container or spill residues thereof. The principal constituent of U151 is metallic mercury.**

\* U.S. EPA, Best Demonstrated Available Technology (BDAT) Background Document for Mercury Wastes, Nov 1989, page 2-18.

\*\* Mercury Treatment and Storage Options Summary Report, A.T. Kearney report for USEPA Reg 5, May 1997, page 1.

## 2.2 What is the Impetus for the Current Study?

### 2.2.1 Land Disposal Restrictions

The Land Disposal Restrictions (LDR) treatment standards established by the 3<sup>rd</sup> 3<sup>rd</sup> Rule (55 *FR* 2250, June 1, 1990) requires roasting and retorting (RMERC) to recovery mercury as the treatment for high-mercury wastes greater than 260 mg/kg mercury. In the 3<sup>rd</sup> 3<sup>rd</sup> Final Rule, EPA cited Congress' preference for "treatment standards to be based on recovery, where possible" (S.Rpt. 98-284, p. 17). In addition, the Agency cited technical reasons for not

promulgating stabilization as the preferred treatment technology for high mercury subcategory wastes. Specifically, data available to support the 3<sup>rd</sup> Final Rule indicated that the metal stabilization agents actually increased the mobility of mercury in the stabilized matrix. Given a growing excess of mercury stocks, as uses of mercury decline, the disposal requirements for excess mercury need to be considered.

### 2.2.2 Defense Logistics Agency Stockpile

The National Defense Stockpile program was established by Congress in the Strategic and Critical Materials Stock Piling Act of 1939, as amended, to minimize the United States' dependence on foreign sources of essential materials in times of national emergency. Between 1949 and 1988, the General Service Administration and Federal Emergency Management Agency were responsible for the program. In 1988, the responsibility for the program was delegated to the Secretary of Defense who assigned the program to the Defense Logistics Agency (DLA). The Defense National Stockpile Center (DNSC) was established within DLA to manage the program. DNSC is headquartered at Fort Belvoir, Virginia and operates storage depots nationwide. The stockpile currently includes 68 commodities, including mercury.

DNSC is responsible for all activities necessary to provide safe, secure, environmentally sound stewardship of all commodities in the National Defense Stockpile. Over the past several years as new technologies have evolved and global economies emerged, Congress has declared most of the Defense National Stockpile materials to be in excess of national defense needs and has authorized their disposition, generally by sale. Mercury is one of these commodities determined to be in excess of national defense needs. In January 2001, DNSC initiated an Environmental Impact Statement (EIS) to solicit comments from the public and policy-makers about what to do with its remaining 11 million pounds of mercury.<sup>3</sup>

The DNSC excess inventory of mercury is “prime virgin” i.e., between 99.5 and 99.9 percent pure mercury. The material is currently stored in steel flasks weighing about 76 pounds (34.5 kilograms). The flasks are stored in wooden pallet boxes. Some of the flasks date from the 1940s and 1950s.

As custodian of the excess inventory of mercury, DNSC must decide on a strategy for management of the material. As required by CEQ and DLA NEPA regulations, this decision must include consideration of a range of reasonable management alternatives and the environmental impacts of those alternatives.

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<sup>3</sup> Memorandum, G. Tracy Mehan, III to Steve Johnson, September 27, 2001, “Developing an EPA Game Plan for Surplus Mercury (draft issue paper).

### 2.3 Bulk Elemental Mercury Treatment Study

The Bulk Elemental Mercury Treatment study was conducted to analyze the effectiveness of commercially available technologies for stabilizing elemental mercury. This study was sponsored by EPA and focuses on the DLA stockpiles. The study started with a solicitation to industry to demonstrate the effectiveness of their stabilization process treatment of elemental mercury. This effort had two major objectives.

1. The first objective was to evaluate alternative processes to RMERC and IMERC for the DLA elemental mercury stores. To that end, a process that will treat an elemental mercury sample to meet a TCLP treatment goal of 0.025 mg/L or less was desired.
2. The second objective was to provide EPA with the treated waste forms for use in empirical testing to compare proposed new analytical protocols to the standard TCLP results, and to assess potential suitable disposal environments for the wastes forms.

Technology vendors participated in this demonstration at their expense, except for the analytical costs incurred from the use of an outside laboratory to perform the surrogate waste characterization, TCLP testing on the treated waste forms, and the costs of shipping the treated waste forms to ALTER, Inc., where the constant-pH leaching was performed.

Sample waste forms from stabilization of elemental mercury were characterized and leached by ALTER, Inc., using both the TCLP and a novel, automated, constant-pH leaching protocol. These data are presented in detail in Section 5. Characterization of the waste forms consisted of bulk density, moisture content, percent organic matter, cation exchange capacity and particle size distribution. These data are presented in Appendix C. Mercury vapor pressure testing will also be performed on the final treated waste. The results of the Oak Ridge National Laboratory testing will be presented in a separate report.



### 3. Detailed Description of Study

#### 3.1 Overall Plan

Mercury contamination exists in various forms, such as soil, sludges, and debris, and in various species, such as organic, inorganic, and elemental. The objective of this investigation is to provide information on the ability of current technologies to convert elemental mercury (or wastes with large components of elemental mercury) into a stable waste form for disposal. Each of the current technologies relies on chemical reactions to minimize volatilization and solubility, as opposed to recovery or separation technologies which generate a near mercury-free residual in addition to concentrated or purified mercury.

EPA and DOE are investigating possible stabilization methods for mercury-contaminated waste and mixed waste streams. These methods are ‘nonthermal,’ occurring at conditions below the boiling point of mercury (about 350°C or 650°F). To investigate the ability of these technologies to effectively treat wastes, EPA designed a detailed project plan (EPA Quality Assurance Project Plan — Technical Support for Amendment of Land Disposal Restrictions for Mercury Wastes, December 2000, Appendix A). EPA requested that several different vendors attempt to treat elemental mercury using their processes identified for the MER 04 project. The resulting treated wastes would each undergo a rigorous set of procedures to better understand the performance of the technology. In addition to reducing mercury mobility, the process should minimize worker exposure, minimize volume increase as waste is treated, minimize secondary waste generation, and maximize operational flexibility.

In completing this project, a coordinated effort was required between technology vendors, laboratories, DOE/ORNL, and EPA. Key participants in the project were as follows:

Treatment technology vendors—Three vendors volunteered to be participants in the study. These vendors participated in the related MER 04 surrogate waste study. Detailed discussion of their roles, technologies, and activities are discussed in Chapter 4 of this report. Responsibilities of the vendors included treating the elemental mercury using bench scale technology, and sending the treated waste back to the laboratory.

The Accelerated Life Testing and Environmental Research Corporation (ALTER), Dillsboro, IN—ALTER’s responsibilities include providing instructions to the vendors, receiving the treated wastes, and conducting leaching tests of the resulting treated wastes. Actual analysis of the treated waste material or leachates for most chemical and physical parameters (including mercury) was conducted by other laboratories. ALTER conducted alkalinity and acidity testing, and pH analysis.

Environmental Enterprises, Cincinnati, OH—Environmental Enterprise was primarily responsible for conducting mercury analysis of solid and aqueous (i.e., leachate) matrices (Appendices B and E).

Agvise Laboratories, Northwood, ND—Agvise was primarily responsible for testing physical

characteristics of the treated waste. These tests include bulk density, moisture content, percent organic matter, cation exchange capacity, and particle size distribution (Appendix C). The Agvise testing uses standard methods for soils, established by the USDA and the Soil Society of America (Appendix D).

Oak Ridge National Laboratory, Oak Ridge, TN—ORNL is responsible for the measurement of the mercury vapor pressure at 20°C and 60°C of treated waste forms. ORNL results will be reported separately.

Activities performed by these parties are described below in more detail. These activities include preparing a surrogate sludge for evaluation and treatment and characterizing both the untreated surrogate sludge and treated residue. Activities relating to the treatment itself are discussed in detail in Section 4 of this report.

#### 3.1.1 Elemental Mercury Preparation

Each vendor was responsible for obtaining elemental mercury for use in the study. Relatively small quantities (less than approximately one kilogram per batch) were generally used by the vendors.

#### 3.1.2 Treated Waste Characterization

The commercial vendors returned the treated material to ALTER for testing. The vendor-treated materials were characterized and subjected to physical and chemical analyses to determine their behavior under a range of potential disposal conditions.

### 3.2 Physical and Chemical Analysis

Samples of the baseline (elemental) mercury and the treated waste generated by the vendors were subjected to a battery of physical and chemical analyses. The technologies used by the vendors are described in Section 4. **Table 3-1** summarizes the analyses conducted on the materials. These testing and analysis procedures are described below:

Baseline untreated mercury: total mercury, TCLP mercury, and constant pH leaching analysis of mercury; physical and chemical analysis at Agvise Laboratory, additional characterization by ALTER.

Treated waste: total mercury, TCLP mercury, and constant pH leaching analysis of mercury; physical and chemical analysis at Agvise Laboratory, additional characterization by ALTER.

In order to assess the stability of the materials, several leaching procedures were performed on the baseline untreated and vendor treated waste. Leaching tests performed by ALTER included the toxicity characteristic leaching procedure (TCLP) and constant pH testing. Upon completion

of each leaching test, the pH of the leachate was recorded and leachate samples sent to Environmental Enterprises Inc for determination of their mercury content. These two leaching tests are discussed below:

**Toxicity Characteristic Leaching Procedure**—This is a standard regulatory test (40 CFR 261.24, SW-846 Method 1311) intended to determine the potential mobility of contaminants in a solid waste under simulated landfill conditions. The TCLP entails exposure of a sample that has been size reduced to pass a 9.5 mm sieve to a 20 fold large volume of acetate buffer for 18 hours.

**Constant pH Leaching**—Constant pH leaching tests are a means to determine the effect of pH on the stability of a waste. The constant pH procedure was developed at ALTER and is attached as Appendix B to the QAPP (presented as Appendix A to this report). Samples are leached in a constant pH solution that is adjusted to, and maintained at, the desired pH end point. The constant pH leaching tests were performed at a minimum of pH values of 2, 4, 6, 8, 10 and 12. The pH is maintained by automated systems for a 14 day period, at which point the resulting leachate is filtered and analyzed for mercury. A nominal 20:1 liquid/solid ratio (20 Kg/1 L) was used in these tests. The longer exposure period of 14 days was selected to ensure equilibrium conditions were obtained.

Table 3-1  
Test Procedures for Bulk Elemental Mercury Project

Parameter	Reference	Laboratory	Matrices
Physical characteristics: density; water content; particle size; cation ion exchange capacity; percent organic matter; cations (magnesium, potassium, calcium, sodium)	Standard Methods for Soils established by the USDA and the Soil Society of America.	Agvise Laboratories	1, 2
Mercury analysis, in leachate and solid matrices	SW 846 Method 7470A	Environmental Enterprises	1, 2; all leachates
Mercury vapor pressure testing	Jerome 431 Arizona Instruments (Phoenix, AZ)	ORNL	2
Alkalinity, acidity	Standard Methods for the Examination of Water and Wastewater	ALTER	2
pH	Standard Methods for the Examination of Water and Wastewater	ALTER	All leachates
Moisture content, particle size	ASTM	ALTER	2
TCLP leaching	SW 846 Method 1311	ALTER	1, 2
Constant pH leaching	—	ALTER	2

Matrices: 1: elemental mercury (untreated).

2: treated waste prepared by each vendor.

\* Only total levels of mercury were to be analyzed in the untreated waste prepared by each vendor.

#### 4. Treatment Technologies

Four waste treatment technology vendors participated in the related MER 04 study. Three of these vendors (identified in this report as Vendors A, B and C) elected to participate in the elemental study. Each of the technologies used by the three vendors involves stabilization and/or amalgamation of the mercury. ORNL and EPA specifically were evaluating technologies which immobilize, rather than separate, mercury within wastes. Data and information concerning these treatment technologies were obtained from the vendor project reports submitted to EPA/ORNL, as well as previously prepared technology or performance descriptions prepared for ORNL.

Detailed descriptions of these technologies are presented in this section of the report. Similarities and differences between the technologies are presented in **Table 4-1**.

Table 4-1  
Summary of Technologies Used for Treatment of Bulk Elemental Mercury

Comparison Factor	Vendor		
	A	B	C
Process Overview	Formation of mercuric sulfide followed by thermoplastic encapsulation using sulfur polymer stabilization/solidification process	Formation of mercuric sulfide with micro- and macroencapsulation	Amalgamation and stabilization process with precipitation of stable salt
Reagents added	95% sulfur polymer, 5% organic modifier, and proprietary additives	Sulfide and proprietary encapsulants	Amalgamation agent and proprietary stabilization reagent
Waste Loading (On dry basis)	33 wt%	Phase I: 55 wt% Phase II: 44 wt%	20.1 wt%
Volume or Weight Increase	203% by weight 1500% by volume	Phase I: 81.8% by weight Phase II: 127% by weight	398% by weight
Final Form of Treated Waste	Monolithic solid	Soil-like and macroencapsulated pellets	Monolithic
Mercury Losses to Air	Estimated 0.3%	None identified	None measured or expected

\* Several vendors use reagents and/or process steps which have been claimed to be confidential business information (CBI). Only non-CBI is presented in this report.

##### 4.1 Vendor A

Vendor A used its proprietary sulfur polymer stabilization/solidification (SPSS) process for treating the elemental mercury. The purpose of this process is to chemically stabilize and physically encapsulate mercury to reduce vapor pressure and leachability. This process is conducted in two stages. The first step is a reaction between elemental mercury and powdered sulfur polymer cement to generate mercuric sulfide (HgS). (Sulfur polymer cement consists of

95 wt-% elemental sulfur reacted with five wt-% of an organic modifier.) During reaction, the vessel is placed under inert nitrogen gas to prevent mercuric oxide (HgO) formation (a compound much more environmentally mobile than mercuric sulfide) and heated to 40°C to enhance the sulfide formation. The purpose of this first step is to chemically stabilize the mercury.

The purpose of the second step is to solidify the product. The mixture is heated to 130°C to melt the thermoplastic sulfur binder. It is then poured into a mold. On cooling, the reacted sulfide particles become microencapsulated within the monolithic sulfur matrix.

Pilot-scale SPSS processing was accomplished using a 1-ft<sup>3</sup>, oil-heated, vertical cone mixer. Mixing action was provided by a 24-inch long auger screw. Feed materials were charged to the unit through a 6-inch diameter port on the cone lid with the auger screw drawing material upward from the base of the cone. When mixing, the system was purged with an inert gas by connection to a regulated nitrogen gas supply. Heat was provided to the jacketed cone by a circulating fluid heat transfer system. A heated ball valve at the base of the cone was used to discharge the molten SPSS product.

Off-gas was controlled by a sequence of a heat exchanger, a liquid nitrogen trap, and HEPA/charcoal filters prior to atmospheric discharge. Vendor A did not measure mercury air releases during processing of the elemental mercury. In earlier demonstrations of treatment of elemental mercury and mercury-contaminated soils, a mercury balance demonstrated that 0.3% of mercury was volatilized and captured in the off-gas collection system.

Vendor A submitted two physical forms of treated waste (both from batch 2) to ALTER for testing. The first waste form was created by allowing the molten material to solidify in bulk. The second waste form submitted for testing by vendor A was pelletized. To prepare the pellets, monolithic material was heated to approximately 140°C and poured into Teflon molds to create small pellets approximately 8-mm in diameter by 8-mm in length. This dimension was selected so that the material would meet the 9.5 mm particle size requirement for TCLP testing. The bulk (monolithic) material was crushed at ALTER, using a commercial compression machine to yield < 9.5mm pieces for parallel TCLP testing. Both the pellet and crushed forms were tested in parallel throughout the evaluation.

#### 4.2 Vendor B

Vendor B used a multi-step process that can be stopped at a given stage dependent on what the performance specification is. The first step (primary stabilization) consists of conversion of elemental mercury to mercuric sulfide (meta-cinnabar). This step fits the EPA definition of elemental mercury amalgamation. The primary product is then subjected to micro and macro encapsulation utilizing a range of polymeric and other agents to attain the desired product specification. For the study in question the final product was a bead-like material that had a top size diameter of 9.5 mm.

On a dry weight basis the primary product contained 55 wt-% elemental mercury. The

product that has been processed through micro and macro encapsulation contained 44 wt-% elemental mercury on a dry weight basis.

#### 4.3 Vendor C

Vendor C used an ambient temperature process, developed to treat elemental, ionic, and complexed forms of mercury in mixed (radioactive and hazardous) waste. Vendor C has previously permitted and operated this process for treatment of mercury-contaminated mixed wastes.

Vendor C placed approximately 1.5 to 2 kg of elemental mercury and reagents inside of a sealed polypropylene bottle. The material was mixed externally (i.e., without a stirrer, propeller, or other internal mechanism). Following treatment of the elemental mercury, each batch remained in the chamber. The final waste form was best described as a monolith which set up within 24 hours. The weight of the treated mercury was increased significantly: for an initial 1.5 to 2 kg mercury, the final weight was 10 kg. This is much greater than the 15 to 20 % increase typically seen for soil treated by the process.

Airborne mercury concentrations were not obtained during this study. Releases are expected to be minimal because all steps following charging of the mercury and reagents (e.g., mixing, setting) are conducted within the sealed bottle.

## 5. Leaching Results

Samples of the treated waste form from each vendor were leached according to both the TCLP and the constant pH leaching protocol, and the concentrations of mercury in both the waste forms and leachate were measured.

Sections 5.1 to 5.3 present the leaching data, by vendor, both as a concentration of mercury in the leachate, and as the percentage of mercury that leached from the treated waste form. The percent mercury calculations are based on the waste loading data provided by the technology vendors, rather than on the measured concentrations of mercury in the waste due to incomplete digestion of the diverse final waste forms. This approach was used because the data indicate a significant negative bias in the analysis of the mercury content of the treated waste forms. Quality control data indicate that the precision and bias of the analysis of mercury in the leachates were acceptable.

### 5.1 Vendor A

Two final waste forms (pellets and crushed material) were evaluated. **Table 5-1** summarizes results for total mercury recovered from the digested solids representing the treated waste form and the TCLP tests. The crushed fraction shows more uniform leaching results (i.e., a relatively lower standard deviation and CV), as expected for a sample with smaller particle size. Also, the pelletized waste is known to be more heterogeneous than the monolith, from which the crushed material came. However, pellet sample 3 is the only solid that met the performance goal of 0.025 mg/L Hg in leachates generated using the TCLP. One replicate of each waste form leached unacceptably in excess of 0.2 mg/L TCLP.

Table 5-1  
Analytical Results for Vendor A  
EEI Work Order 01-07-213

TCLP							
Pellets				Crushed			
Sample	pH	TCLP (mg/L)	Percent Leached	Sample	pH	TCLP (mg/L)	Percent Leached
1	5.18	0.0580	0.0004	1	4.98	0.144	0.0009
2	5.22	1.13	0.0068	2	4.97	0.0493	0.0003
3	5.22	0.0243	0.0001	3	4.98	0.202	0.0012
Average		0.404	0.0024	Average		0.132	0.0008
Std. Dev.		0.629	-	Std. Dev.		0.0771	-
CV		155	-	CV		58.4	-

The amount of mercury recovered by the TCLP test is reported as percent leached, and is based on the waste loading in the solid sample. Percent leached is calculated as follows:

$$[(\text{mg Hg/L leachate})/(\text{mg Hg/kg sample}/20)] * 100$$

where mg Hg/L is the TCLP result, mg Hg/kg sample is the mercury concentration in the solid, based on the vendor's waste loading, and 20 is the liquid / solid ratio of the leaching test.

Results for the constant pH leach tests are tabulated in **Table 5-2** and plotted on **Figure 5-1** with the TCLP results. For this waste form, the constant pH results at pH 4 and 6 are similar to the TCLP results obtained at pH ~4.98.

Table 5-2  
Constant pH Leaching Results for Vendor A  
EEI Work Order 01-07-213 & 01-10-360

pH	Pellets			Crushed			RPD Sample Dups.
	Hg conc. (mg/L)	Percent Leached <sup>1</sup>	Leachate volume <sup>2</sup> (mL)	Hg conc. (mg/L)	Percent Leached <sup>1</sup>	Leachate volume <sup>2</sup> (mL)	
2	0.00542	0.000034	511.59	0.00658	0.00004	512.69	P – 86.6
2	0.0137	0.000091	546.80	0.0132	0.00008	509.88	C – 66.9
4	0.984	0.006136	514.48	0.0621	0.00042	552.00	-
6	0.0835	0.000511	504.43	16.7	0.11135	550.06	-
8	44.9	0.274293	503.99	30.8	0.22007	589.46	P – 59.5
8	24.3	0.148242	503.29	53.5	0.36116	556.93	C – 53.9
9	13.7	0.085078	512.33	-	-	-	-
10	0.0742	0.000499	555.21	0.0839	0.00054	531.59	-
11	0.00951	0.000063	550.01	-	-	-	P – 60.2
11	0.0177	0.000121	561.98	-	-	-	C - NA
12	127	0.773669	502.58	74.6	0.53159	587.88	P – 19.9
12	155	1.031492	549.02	23.5	0.20415	716.68	C - 104
2	< 0.00050	-	501.81	< 0.00050	-	506.14	Blank

<sup>1</sup> Calculated based on the waste loading in the solids.

<sup>2</sup> Total volume of leachate, including addition of NaOH and/or HNO<sub>3</sub>



Figure 5-1  
Constant pH Leaching Results for Vendor A  
Concentration Leached

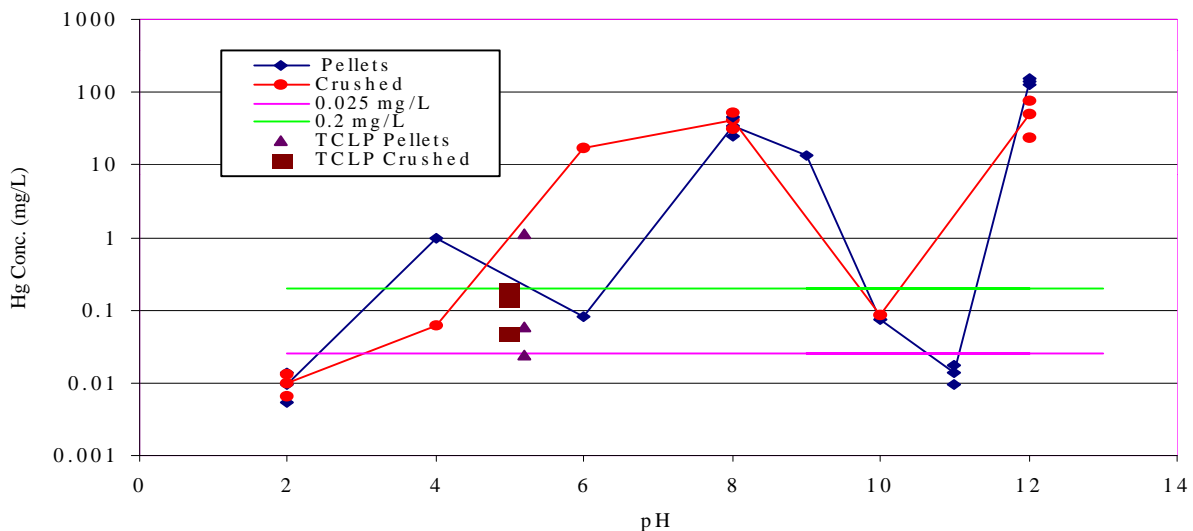
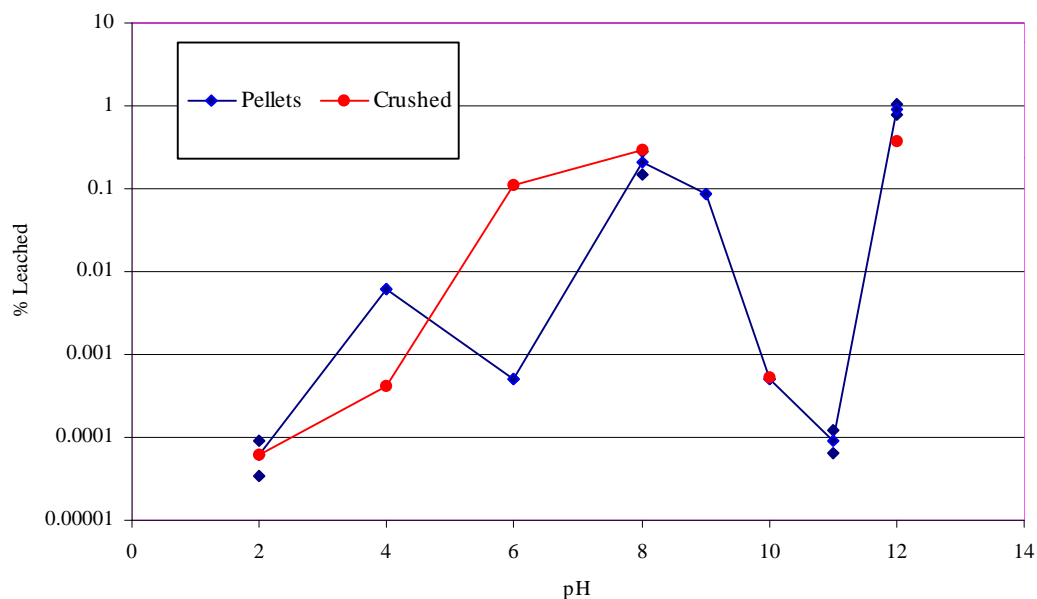


Table 5-2 reports the analytical results, the amount of mercury leached from the solid (percent leached), and the total volume of leachate fluid after addition of reagents to maintain the indicated pH. Duplicates were run at pH values of 2, 8 and 11 (pellets only) and 12. Percent leached is calculated according to the equation presented for the TCLP results. Relative percent difference (RPD) for the experimental duplicates do not meet the QA criteria of  $\pm 50$  percent, with the exception of the pellet duplicates at pH 12. The duplicate values appear with the calculated average on Figure 5-1 and **Figure 5-2**, and the trend is drawn through the calculated average. Additional tests for the pellet samples were run at pH 9 and 11 to investigate the sharp decrease in mercury concentration at pH 10.

Percent leached is calculated according to the equation presented for the TCLP results using the leachate volume in Table 5-2 to calculate the liquid/solid ratio. Values in Table 5-2 indicate that 0.11 to 0.53 percent of the original mercury treated is leached from the crushed solid at pH 6, 8, and 12, which did not undergo recasting. Much smaller losses were observed at pH 2, 6, and 10.

A comparison of the results for pellets and crushed samples shows that mercury concentrations are similar at pH 2, 8, 10 and 12, and quite different at pH 4 and 6. Laboratory QA/QC (Appendix E) indicates the analytical results are valid as reported. Samples representing the pellets plot as a saw tooth pattern, and the crushed samples show increasing mercury values up to pH 8 followed by a decrease and then an increase to pH 12. The additional pellet samples run at pH 9 and 11 indicate the minimum at high pH lies near 11, rather than 10.

Figure 5-2  
Constant pH Leaching Results for Vendor A  
Percent Leached



## 5.2 Vendor B

Vendor B provided both an intermediate (Phase I) and final waste form (Phase II). Only the final waste form was used in the TCLP tests. The data from the TCLP analyses are presented in **Table 5-3**. The mercury concentrations in the TCLP leachates were below the performance goal of 0.025 mg/L Hg.

Table 5-3  
Analytical Results for Vendor B  
EEI Work Order 01-12-039

TCLP							
Phase I				Phase II			
Sample	pH	TCLP (mg/L)	Percent Leached <sup>1</sup>	Sample	pH	TCLP (mg/L)	Percent Leached <sup>1</sup>
1	5.53	-	-	1	4.84	0.00588	0.000027
2	5.63	-	-	2	4.84	0.00611	0.000028
3	5.79	-	-	3	4.78	0.00284	0.000013
-		-	-	4	4.81	0.00613	0.000028
-		-	-	-		-	-
Average		-	-	Average		0.00524	0.000024
Std. Dev.		-	-	Std. Dev.		0.00183	-
CV		-	-	CV		34.8	-

<sup>1</sup> Calculated based on the waste loading of the solids.

Phase II results for the constant pH leach tests are tabulated in **Table 5-4**, and plotted on **Figure 5-3** on a concentration basis with the TCLP results, and in **Figure 5-4** as a percentage of mercury that leached. Table 5-4 reports the analytical results, the amount of mercury removed from the solid (percent leached), and the total volume of leaching fluid, including the volume of reagents added to maintain the indicated pH. Duplicates were run at pH values of 2, 8 and 12, with the RPD at pH 2 and 8 meeting the QA criteria and the results at pH 12 failing. The duplicate values appear with the calculated average on Figures 5-3 and 5-4, and the trend is drawn through the calculated average. Laboratory QA/QC (Appendix E) indicates the analytical results are valid as reported.

Table 5-4  
Constant pH Leaching Results for Vendor B  
EEI Work Order 01-12-039

Phase II				
pH	Hg conc. (mg/L)	Percent Leached <sup>1</sup>	Leachate Volume <sup>2</sup> (mL)	RPD Sample Dups.
2	0.00105	0.000005	550.62	39.1
2	0.00156	0.000007	500.28	
4	0.00186	0.000009	504.97	
6	0.00484	0.000022	501.29	
8	0.0110	0.000050	503.34	27.7
8	0.00832	0.000038	501.45	
10	0.0118	0.000056	525.30	
12	0.143	0.000665	511.34	72.1
12	0.0672	0.000317	518.18	
2	< 0.00050	-	500.77	Blank

<sup>1</sup> Calculated based on the average total mercury concentration in Phase II solids.

<sup>2</sup> Total volume of leachate, including addition of NaOH and/or HNO<sub>3</sub>

The mercury concentration increases by two orders of magnitude as the pH climbs from 2 to 12 (Figure 5-3). A very small fraction of the total mercury is released from the solids, which is in agreement with results from the TCLP tests. The volume of reagent added to each test does not appear to effect the result. Duplicates at pH 2 show a gross difference in the amount of reagent added to each, yet the mercury concentrations are similar. This is the likely result of solubility limited conditions.

Figure 5-3  
Constant pH Leaching Results for Vendor B  
Concentration Leached

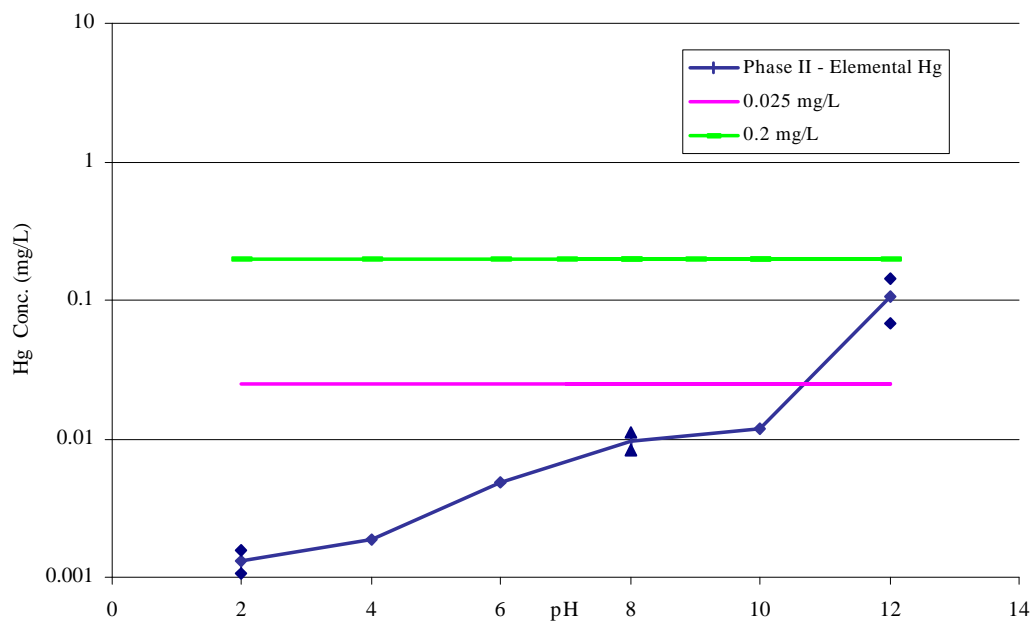
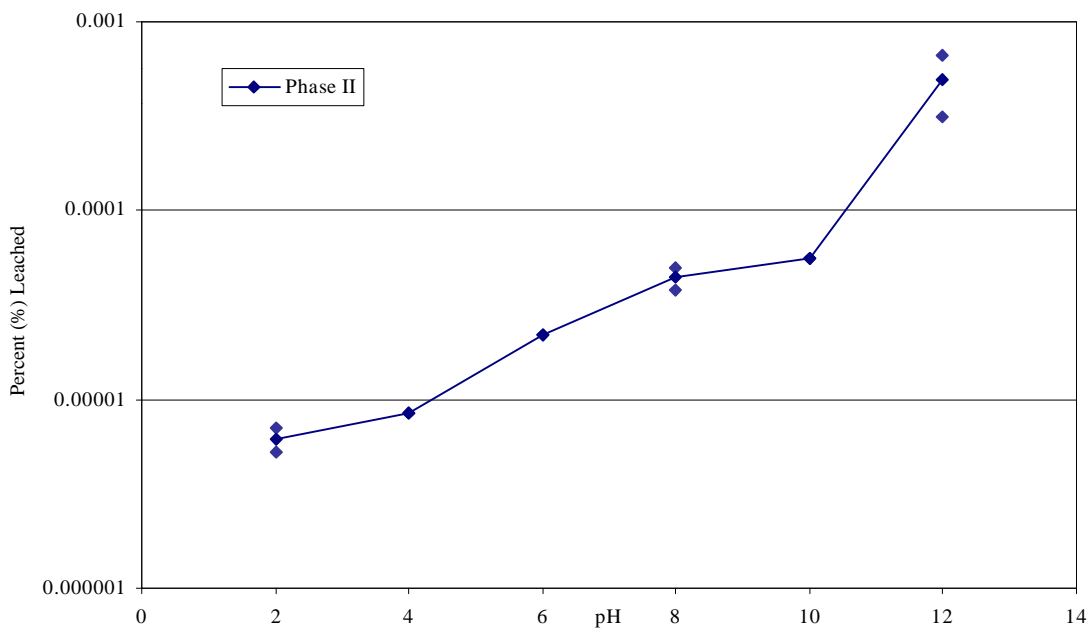


Figure 5-4  
Constant pH Leaching Results for Vendor B  
Percentage Leached



### 5.3 Vendor C

**Table 5-5** summarizes the TCLP results for of a treated waste form produced by Vendor C. Relative to Vendors A and B, there is considerably less variation in the mercury concentration between the sample aliquots, as demonstrated by the reported standard deviation and coefficient of variation (CV). The TCLP tests yielded mercury concentrations that met the performance goal of 0.025 mg/L Hg by the TCLP.

Table 5-5  
Analytical Results for Vendor C  
EEI Work Order 01-08-371

TCLP			
Sample	pH	TCLP (mg/L)	Percent Leached <sup>1</sup>
1	6.67	0.0129	0.00013
2	6.67	0.0133	0.00013
3	6.70	0.0152	0.00015
4	6.70	0.0154	0.00015
-		-	-
Average		0.0142	0.00014
Std. Dev.		0.00128	-
CV		9.04	-

<sup>1</sup> Calculated based on the waste loading of mercury in the treated waste form

Results for the constant pH leach tests are tabulated in **Table 5-6** and plotted in **Figure 5-5** with the TCLP results. For this waste form, the constant pH results at pH 6 and 8 are greater than the TCLP results obtained at pH ~6.7. This indicates that the TCLP likely did not reach equilibrium for this matrix during its 18-hour exposure period.

Table 5-6 reports the analytical results, the amount of mercury removed from the solid (percent leached), and the total volume of leachate, including the reagents added to maintain the indicated pH. Duplicates were run at pH values of 2, 8 and 12, with the RPD at pH 2 and 12 meeting the QA criteria and the results at pH 8 exceed the desired criteria. This may be attributed to sample heterogeneity. The duplicate values appear with the calculated average on Figure 5-5 and **Figure 5-6**, and the trend is drawn through the calculated average. Laboratory QA/QC indicates the analytical results are valid as reported. The mercury concentration decreases by three orders of magnitude as the pH climbs from 2 to 12 (Figure 5-5).

Table 5-6  
Constant pH Leaching Results for Vendor C  
EEI Work Order 01-08-371 & 01-10-360

pH	Hg conc. (mg/L)	Percent Leached <sup>1</sup>	Leachate Volume <sup>2</sup> (mL)	RPD Sample Dups.
2	29.7	0.39069	661.02	6.25
2	27.9	0.36725	661.44	
4	0.315	0.00393	626.71	
6	0.0323	0.00032	501.32	
8	0.0494	0.00049	500.93	153
8	0.368	0.00367	500.72	
10	0.139	0.00145	524.17	
12	0.0251	0.00028	566.20	0.80
12	0.0249	0.00025	501.09	
2	0.00066	-	506.86	Blank

<sup>1</sup> Calculated based on the waste loading of mercury in the treated waste form

<sup>2</sup> Total volume of leachate, including addition of NaOH and/or HNO<sub>3</sub>

Figure 5-5  
Constant pH Leaching Results for Vendor C  
Concentration Leached

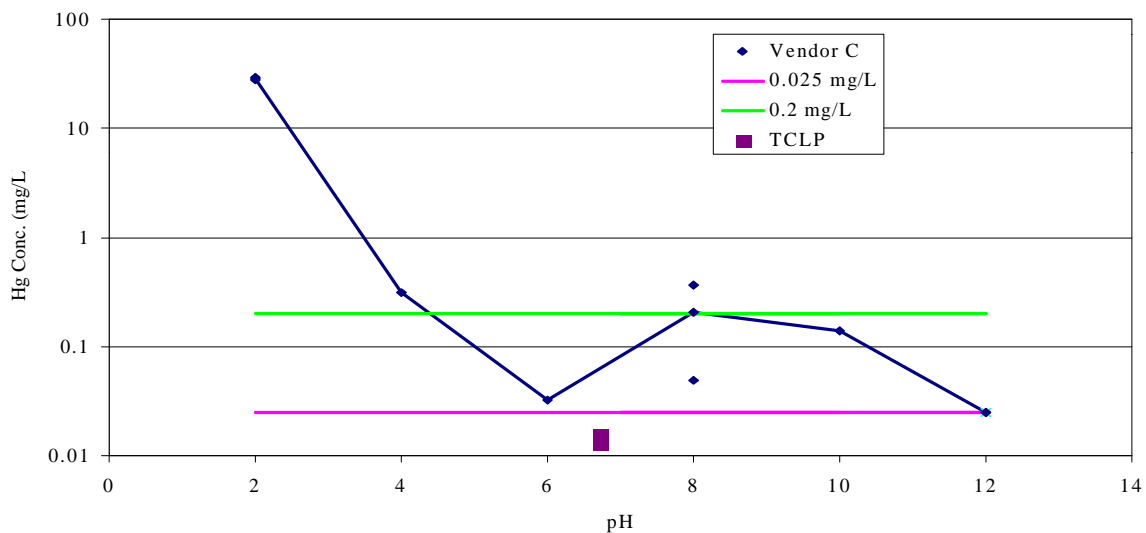
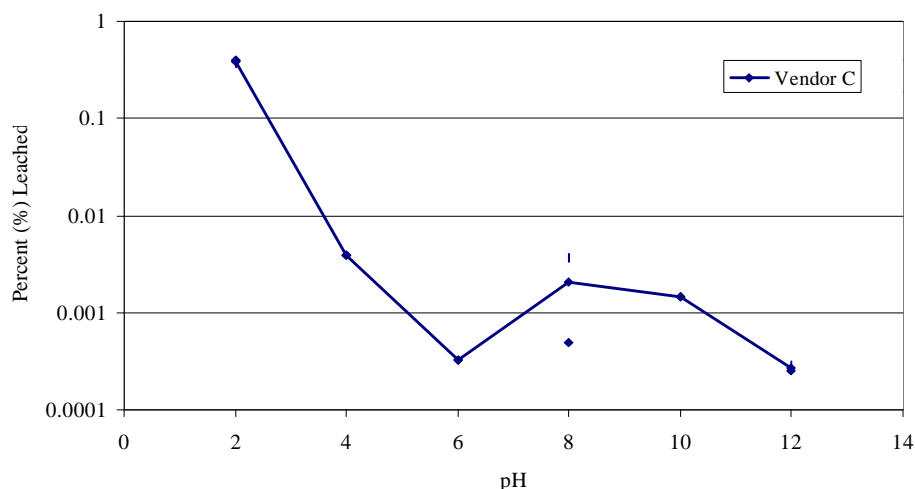


Figure 5-6  
Constant pH Leaching Results for Vendor C  
Percentage Leached



#### 5.4 Mercuric Selenide

A process to convert mercury into mercuric selenide ( $\text{HgSe}$ ) has been developed by Bjasta Atervining A B, Bjasta Sweden. In the process, mercury and selenium are heated and allowed to react in the vapor phase to yield a mercuric selenide powder when cooled. In order to assess the leachability of this type of treated wasteform over the range of pH values expected at a RCRA Subtitle C landfill, reagent mercury selenide was obtained and subjected to constant pH leaching at pH 7 and pH 10, and again at pH 7 and pH 10 with 500 ppm of chloride present in the leachate.

While mean ground water chloride concentrations are approximately 160 mg/L, landfill leachates range from 59 to 6560 mg/L in industrial landfills and 96 to 31,100 mg/L in hazardous waste landfills.<sup>4</sup> Because mercury chloride is a soluble mercury species, these initial runs were performed to explore the effects of chloride on the solubility of mercury selenide.

The constant pH leach tests are tabulated in **Table 5-7**, and plotted on **Figure 5-7** on a concentration basis with the TCLP results, and in **Figure 5-8** as a percentage of mercury that leached. At pH 7, the addition 500 ppm of chloride increased solubility approximately three fold and almost four fold at pH 10. This indicates that the major ions present in a given disposal environment may significantly impact the release from the treated waste form and must also be considered in the evaluation of suitable disposal sites in addition to pH and redox conditions.

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<sup>4</sup>Characterization and Evaluation of Landfill Leachate (Draft), SAIC, Reston, VA, September 2000.

Table 5-7  
Constant pH Leaching Results for Mercury Selenide

pH	Hg conc. (mg/L)	Percent Leached <sup>1</sup>	Leachate volume <sup>2</sup> (mL)
7	0.00656	0.000018	501.93
7 (Cl)	0.0216	0.000060	500.98
10	0.0278	0.000308	528.84
10 (Cl)	0.108	0.000082	512.39
10 (Blank)	<0.00050		500.24

<sup>1</sup> Calculated based on the mass of mercury in the mercury selenide reagent

<sup>2</sup> Total volume of leachate, including addition of NaOH and/or HNO<sub>3</sub>

Figure 5-7  
Constant pH Leaching Results for HgSe  
Concentration Leached

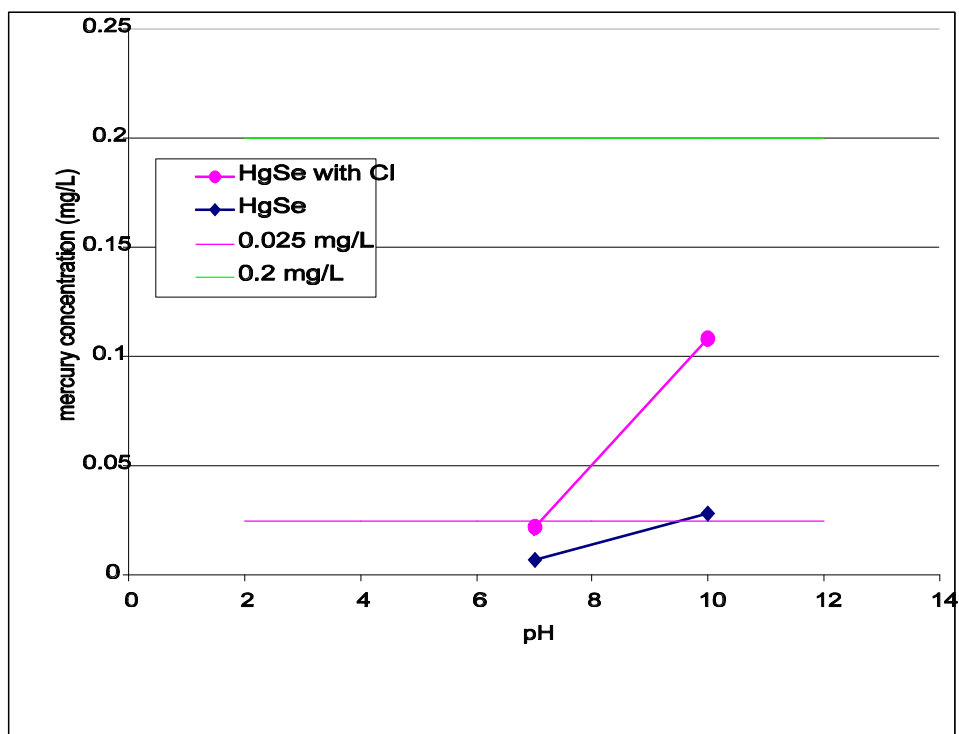
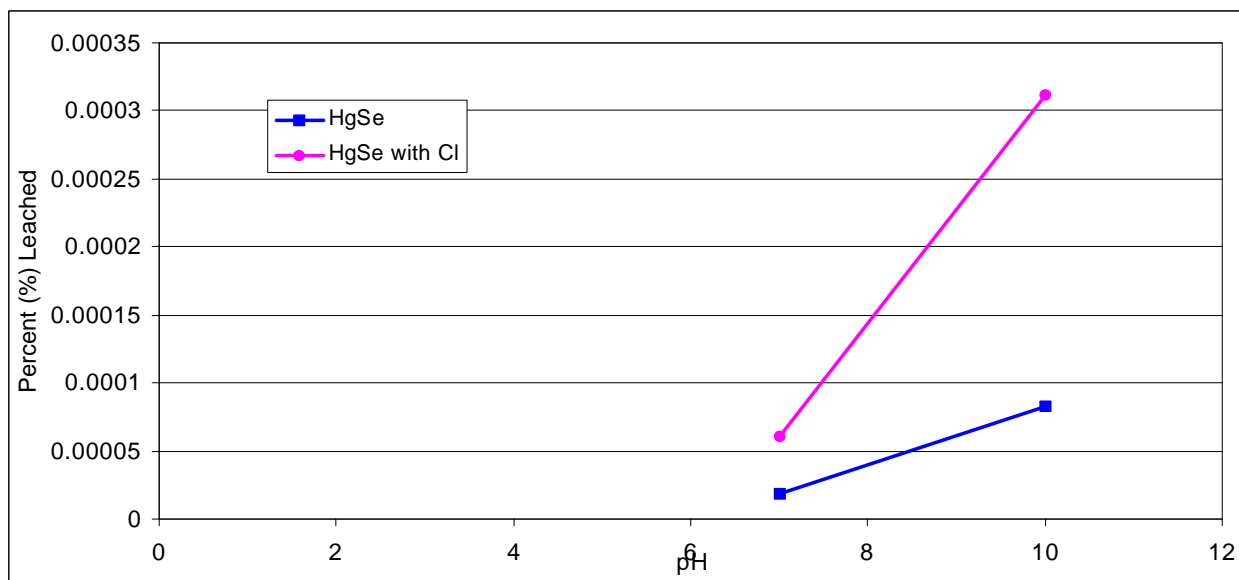




Figure 5-8  
Constant pH Leaching Results for HgSe  
Percentage Leached



## 5.5 Conclusions

**Figure 5-9** provides the constant pH leach test data discussed previously for all three vendors, plotted on a concentration basis. **Figure 5-10** provides the same data, plotted as a percentage of mercury that leached from the treated waste forms. From these Figures, it is evident that the stability of the mercury in the treated waste forms varies widely across the pH range tested. For example, Vendor A's treated waste form performed better at pH 2 and 10-11, than at the other pHs tested. Vendor B's treated waste form performed best at low pH, while Vendor C's waste form leached less mercury at high pH than at low pH. Clearly, the stability of mercury in these treated waste forms will be highly dependant on the disposal conditions. The combination of site-specific disposal conditions and appropriate treatment technology must be considered as decisions are made about disposal of waste bulk elemental mercury.

Figure 5-9  
Constant pH Leaching Results for All Vendors  
Concentration Leached

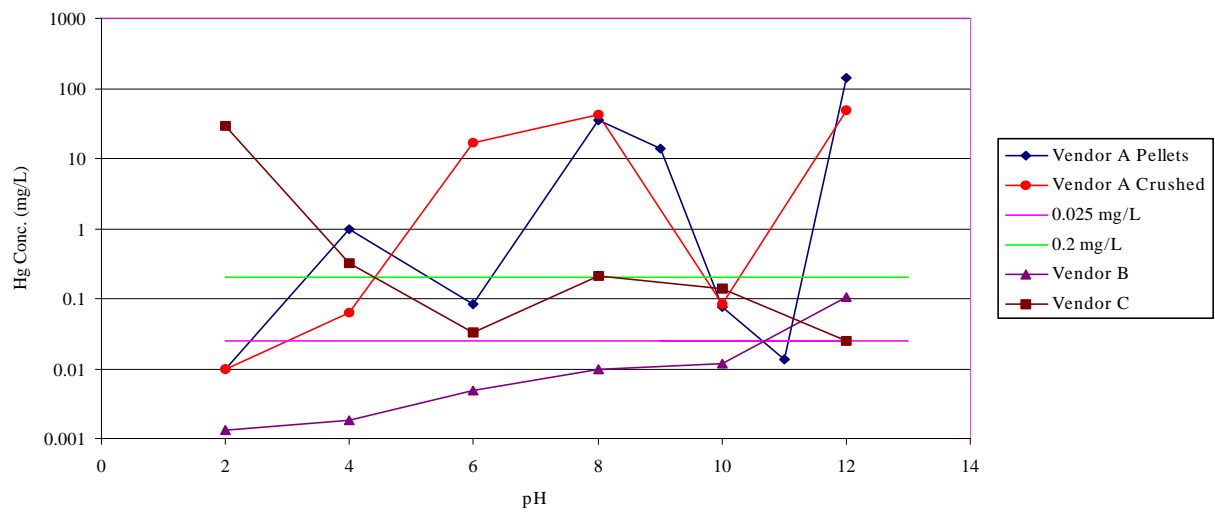
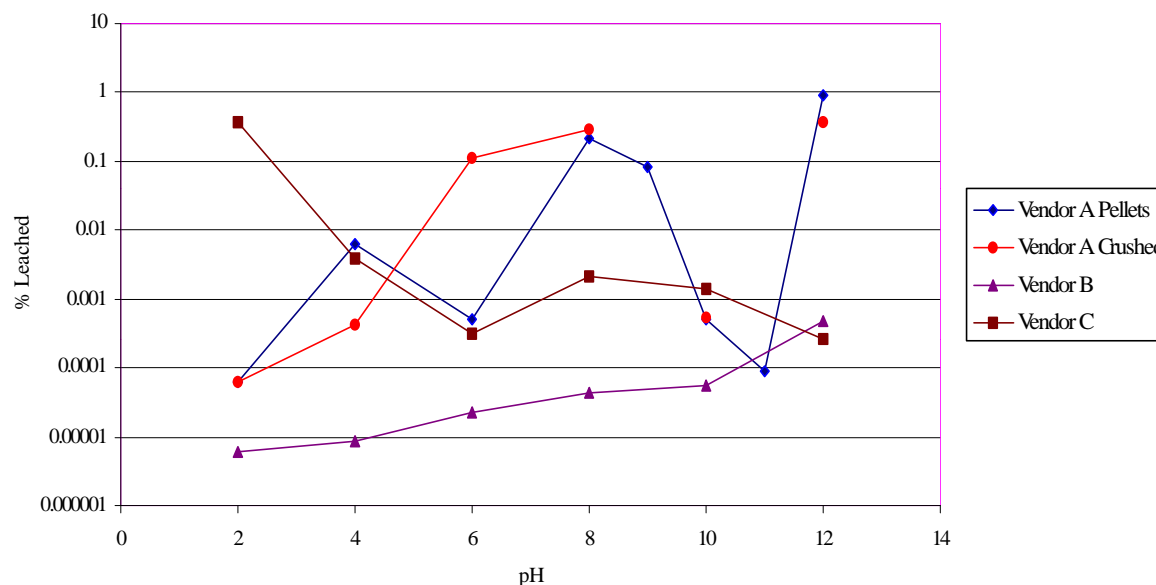


Figure 5-10  
Constant pH Leaching Results for All Vendors  
Concentration Leached



## 5.7 Additional Information Resources

The following articles are relevant to this topic:

“Stabilization/solidification (S/S) of mercury-containing wastes using reactivated carbon and Portland cement”, Zhang, Jian; Bishop, Paul L. Journal of Hazardous Materials (2002), 92(2), 199-212.

“Sulfide-induced stabilization and leachability studies of mercury containing wastes”, Piao, Haishan; Bishop, Paul, Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002 (2002), ENVR-207.

“Phosphate-induced mercury stabilization”, Zhang, Jian; Bishop, Paul L., Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry (2001), 41(1), 422-424.

“Sulfide-induced mercury stabilization”, Piao, Haishan; Bishop, Paul L., Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry (2001), 41(1), 428-431.

“Stabilization of radioactively contaminated elemental mercury wastes”, Stewart, Robin; Broderick, Tom; Litz, John; Brown, Cliff; Faucette, Andrea., Proceedings of the International Conference on Decommissioning and Decontamination and on Nuclear and Hazardous Waste Management, Denver, Sept. 13-18, 1998 (1998), 3 33-36.

“Mercury stabilization in chemically bonded phosphate ceramics”, Wagh, Arun S.; Jeong, Seung-Young; Singh, Dileep, Ceramic Transactions (1998), 87(Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries III), 63-73.

“A Framework for Risk Assessment of Disposal of Wastes Treated by Solidification/Stabilization”, Batchelor, B., Environmental Engineering Science, 14(1): 3-13, 1997.

“A study of immobilization of four heavy metals by solidification/stabilization with Portland cement”, Susan A. Trussell, Ph.D. Dissertation, Texas A&M University, College Station, Texas, 1994.

“Immobilization of chromium and mercury from industrial wastes”, Wasay, S. A.; Das, H. A. , J. Environ. Sci. Health, Part A (1993), A28(2), 285-97.

Chemical Fixation and Solidification of Hazardous Wastes, Jesse R. Conner, Van Nostrand Reinhold, New York, 1990.

“An investigation of mercury solidification and stabilization in portland cement using x-ray photoelectron spectroscopy and energy dispersive spectroscopy”, McWhinney, Hylton G.; Cocke, David L.; Balke, Karl; Ortego, J. Dale., Cem. Concr. Res. (1990), 20(1), 79-91.

“Studies of zinc, cadmium and mercury stabilization in OPC/PFA mixtures”, Poon, C. S.; Perry, R., Mater. Res. Soc. Symp. Proc. (1987), 86(Fly Ash Coal Convers. By-Prod.), 67-76.

“Permeability study on the cement based solidification process for the disposal of hazardous wastes”, Poon, C. S.; Clark, A. I.; Perry, R.; Barker, A. P.; Barnes, P., Cem. Concr. Res. (1986), 16(2), 161-72.

“Mechanisms of metal fixation and leaching by cement based fixation processes”, Poon, C. S.; Clark, A. I.; Peters, C. J.; Perry, R., Waste Manage. Res. (1985), 3(2), 127-42.

“Mechanisms of metal stabilization by cement based fixation processes”, Poon, C. S.; Peters, C. J.; Perry, R.; Barnes, P.; Barker, A. P., Sci. Total Environ. (1985), 41(1), 55-71.